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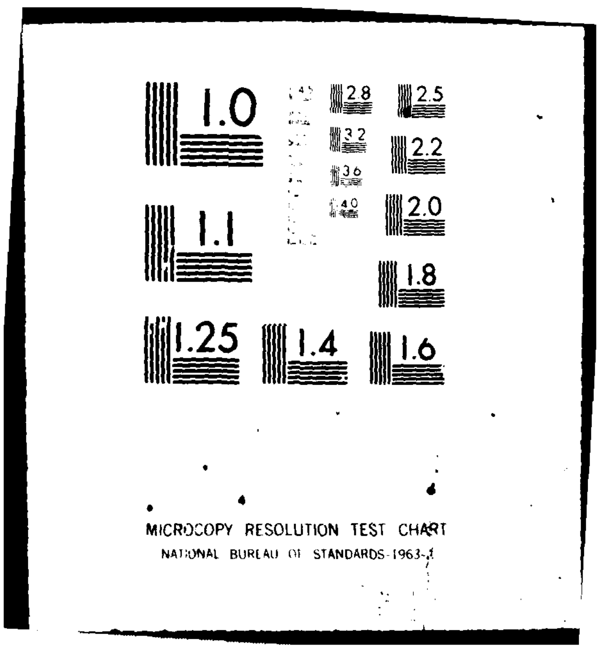
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Crystal Structure and Properties of Tetrathiafulvalenium Triiodide

by

Robert C. Teitelbaum,[1a, b, c] Tobin J. Marks*[1a, 2] and Carroll K. Johnson[1d]

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Slow cooling of a hot acetonitrile solution of tetrathiafulvalene (TTF) and iodine yields a mixture of crystalline products including monoclinic crystals of high iodine composition: $TTF \cdot I_3$. A single crystal X-ray structure analysis has been carried out on these crystals of symmetry $P2_1/n$ with 4 molecules per unit cell. The cell parameters are $a = 9.411(2)$ Å, $b = 18.787(3)$ Å, $c = 7.771(1)$ Å, $\beta = 103.2(1)$, and $V = 1374(1)$ Å^3. The structure consists of integrated stacks along the ⟨102⟩ axis with TTF^+ dimers interspersed between pairs

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Contribution from the Department of
Chemistry and the Materials
Research Center
Northwestern University
Evanston, Illinois 60201 and
the Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

CRYSTAL STRUCTURE AND PROPERTIES OF TETRATHIAFULVALENIUM TRIIODIDE

by Robert C. Teitelbaum,[1a, b, c] Tobin J. Marks*[1a, 2] and Carroll K. Johnson*[1d]

ABSTRACT

Slow cooling of a hot acetonitrile solution of tetrathiafulvalene (TTF) and iodine yields a mixture of crystalline products including monoclinic crystals of high iodine composition: $TTF \cdot I_3^-$. A single crystal X-ray structure analysis has been carried out on these crystals of symmetry $P2_1/n$ with 4 molecules per unit cell. The cell parameters are $\underline{a}$ = 9.411(2) Å, $\underline{b}$ = 18.787(3) Å, $\underline{c}$ = 7.771(1) Å, β = 103.2(1), and V = 1374(1) Å^3. The structure consists of integrated stacks along the

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$\langle 102 \rangle$ axis with TTF^+ dimers interspersed between pairs of triiodide ions. Consistent with the structural results, single crystal measurements indicate that this material exhibits high electrical resistivity with $\sigma_{RT} < 9 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$.

INTRODUCTION

Considerable attention in recent years has been focused on the chemistry and physics of materials which exhibit highly anisotropic electrical, optical, and magnetic properties.[3] Of particular interest have been organic and metal-organic solids which exhibit metal-like charge transport along one crystalline axis. The discovery of the "organic metal" tetrathiafulvalene-tetracyanoquinodimethane, TTF-TCNQ, prompted a number of studies of TTF as an electron donor and precursor for other highly conductive solids. Halogen oxidation, for example, yields a variety of charge transfer salts.[4]

One direction of activity in our Laboratories and others has involved the iodine-containing TTF salts, $TTF \cdot I_x$. The stoichiometries prepared to date range from x=0.71 to 3.0, but detailed single crystal characterization has been restricted to a limited number of low iodine phases. The most conductive of these is $TTF \cdot I_{0.71}$ [4a, b] with a room temperature conductivity of ca. 300 Ω^{-1} cm^{-1} along the needle axis. This material possesses an ordered, modulated crystal structure containing stacks of eclipsed, partially oxidized TTF[4b] molecules, and parallel chains of I^- ions.[4h, 5] Two additional phases of intermediate stoichiometry with x $\sim$ 2.0 have been isolated which vary only in the degree of order-disorder. The first $TTF \cdot I_2$ structure (space group Immm) contains disordered chains of triiodide ions and disordered TTF stacks $((TTF^{+0.7})(I_3^-)_{0.7})$.[4g, 6, 7] Preliminary X-ray crystallographic investigations suggest that the second $TTF \cdot I_2$ phase(space group Fddd) is a superstructure of the first $TTF \cdot I_2$ phase with ordered TTF stacks,but again with disordered triiodide ions.[6,7] Full expositions of the $TTF \cdot I_2$ structures, spectroscopy and transport properties are in preparation. In view of the accumulating knowledge on the above TTF-iodine complexes, it would clearly be of interest to investigate, for comparative purposes, the phase of greatest iodine content. This would provide information on how the crystal structure,[8] degree of partial oxidation, and transport properties adjust to the increased dopant level. Such information might also shed light on how large amounts of iodine are sometimes accomodated in metal glyoximate[9] and phthalocyanine[10] lattices. Here, again, phases with very high iodine content have been isolated.[9,10] We report here the synthesis, X-ray diffraction structure determination, and single crystal conductivity of the high iodine TTF phase, $TTF \cdot I_3$.

EXPERIMENTAL

Synthesis of $TTF \cdot I_3$. Tetrathiafulvalene triiodide was prepared under a nitrogen atmosphere by adding dropwise a solution of 80 mg (0.39 mmole) TTF (Aldrich Chemical Co.) in 10 ml acetonitrile (freshly distilled from P_2O_5 under nitrogen), to a stirring solution of 120 mg. (0.47 mmole) triply sublimed I_2 in 10 ml of freshly distilled acetonitrile. Sufficient acetonitrile was added until the total volume was 50 ml . The solution was heated to 50° C with constant stirring until all of the solid present dissolved. Upon slow cooling to room temperature, a mixture of crystals of $TTF \cdot I_{0.71}$, $TTF \cdot I_2$, and in trace amounts, $TTF \cdot I_3$ resulted. The product was then washed with freshly distilled benzene and dried with a stream of nitrogen. The morphology of the $TTF \cdot I_3$ crystals are sufficiently different from the other phases to be easily separated by inspection. Insufficient quantities of material were obtained for elemental analysis.

X-ray Diffraction Study. $TTF \cdot I_3$ has 4 molecules per unit cell with space group symmetry $P2_1/n$. Least-squares refinement of cell parameters using 10 high order reflections gave the unit cell dimension $\underline{a}$ = 9.411(2), $\underline{b}$ = 18.787(3), and $\underline{c}$ = 7.771(1) Å, with β = 103.2(1)° and V = 1374(1) Å^3.

Single crystal intensities from a polyhedral crystal were collected on the Oak Ridge computer-controlled diffractometer using filtered molybdenum radiation. Of the 3915 unique reflections measured, 3284 had intensities greater than one sigma. A twin or perhaps an unidentified second phase was present and caused at least 75 reflections, mainly in the (hk0)zone, to have excessive observed intensity. The (0k0) reflections were all affected. An absorption correction applied to the data gave transmittancy factors of 0.13 to 0.17.

Structure Solution and Refinement. The three iodine atom positions were found using the direct-methods program MULTAN of Germain, Main and Woolfson.[11] These matched the heavy-atom vectors of the Patterson map. The sulfur and carbon atoms were then found using a Fourier map computed with phases based on iodine atom positions. The four hydrogen atoms were placed in idealized positions and their positional parameters included in the refinement.

Refinement of all nonhydrogen atoms with anisotropic thermal motion and hydrogen atom positions led to an R index of 0.078 on F^2 for all 3915 reflections. The refinement was based on 3090 reflections with 75 reflections deleted because of the twinning probelm and reflections $<$ 1.5 sigma omitted. The $R(F^2)$ index for the reflections used in the refinement was 0.054. Tables of the final $|F_o|$ and $|F_c|$ values for the 3915 reflections are available upon request.[12]

Atomic scattering factors for S, C, H, and the central I were taken directly from the International Tables of X-ray Crystallography, Volume IV.[13] Scattering factors for the two outer iodines in the triiodide were taken as the average of the scattering factors for I° and I^{-}, since it has been shown that the negative charge in the triiodide ion is distributed among the outer iodines, while the central iodine is approximately neutral.[9a, 14] The real and imaginary anomalous-dispersion scattering-factor correlation of Cromer and Liberman[15] were included.

Electric Conductivity Measurements. The samples examined for dc conductivity studies (using the apparatus described previously[9]) were nearly hexagonal prisms, with all dimensions on the order of a few tenths of a millimeter. The small crystal size permitted only two probe conductivity measurements, though orientations both parallel and perpendicular to the hexagonal plane could be examined. Samples were mounted by pressure contact between two spring-loaded brass pins.

RESULTS AND DISCUSSION

The reaction of TTF with iodine in acetonitrile, followed by slow cooling, yields $TTF \cdot I_x$ phases of various stoichiometries (see Experimental Section for methodology). The small quantities of $TTF \cdot I_3$ crystals formed were mechanically separated from the other phases.

Description of the Structure. The final atomic coordinates and anisotropic temperature factors are given in Table I. A stereoscopic view of the unit cell contents is shown in Figure 1 and the I_3^- ion close contacts are illustrated in Figure 2. The crystal structure consists of integrated stacks of cofacial TTF^+ dimers in alternation with pairs of triiodide ions. The TTF^+ cation is distorted somewhat from planarity, with all sulfur atoms 0.01-0.03 Å below (i.e. toward the other molecule of the dimer) and all carbon atoms 0.0-0.03 Å above the least-squares best plane. The spacing between least-squares best planes for the TTF^+ ions within the dimer is 3.40(1) Å, but the S-S distances of 3.351(2) and 3.373(2) Å are somewhat shorter. The molecular packing in $TTF \cdot I_3$ is reminiscent of that communicated for $TTF \cdot Br$ (and isomorphous $TTF \cdot Cl$), also integral oxidation state salts.[4i, j, 16] In these materials, integrated stacks of $(TTF)_2^{+2}$ dimers and halide ions also occur. The interplanar spacing between members of the dimer appears to be somewhat larger in the present case (3.40(1) Å) than in $TTF \cdot Br$ (3.34 Å).[4i, j, 16]

These interplanar spacings are considerably shorter than the TTF spacings of 3.55 (1) Å found in the segregated stack structures of $TTF \cdot I_{0.71}$ and $TTF \cdot I_2$. The spacings in the present case are also shorter than in the eclipsed $(TTF)_2^{+2}$ dimers of $(TTF)_2Ni(S_4C_4H_4)$ (here the S-S distance is given as 3.48 Å).[17] The direct axis fractional components of the TTF^+ plane normal in $TTF \cdot I_3$ are (0.0679, -0.0099, 0.1166) which is approximately along the <102> direction. The TTF^+ ions are almost exactly superimposed with a slight lateral offset of about 0.25 Å perpendicular to the long axis of the molecule.

The molecular structural parameters for $TTF \cdot I_3$ are summarized in Table II. In Figure 3, the bond distances and angles within the tetrathiafulvalenium ion are illustrated. These indicate that the cation is rather symmetrical, even though this is not required by the crystallographic symmetry. A comparison of the TTF^+ structural data with that of other TTF cations as well as with neutral TTF is set out in Table III. It can be seen that oxidation is accompanied by lengthening of the exocyclic double bond (a) and shortening of the contacts between the two carbon atoms involved in the exocyclic double bond and the sulfur atoms (b). The metrical parameters for TTF^+ in the present study are experimentally indistinguishable from those in $TTF \cdot Br$.[16]

The $TTF \cdot I_3$ crystal structure also contains parallel, zig-zagging chains of triiodide ions. The arrangement of the triiodide ions is illustrated in Figure 2. The triiodide ion deviates slightly from linearity with an I-I-I angle of 175.40(2)°. This slight bending is frequently observed in structures of triiodides (Table IV) and reflects the rather flat potential energy surface for molecular distortion.[18] The fact that the terminal iodine atoms of the I_3^- ion are slightly displaced toward the positively charged $(TTF)_2^{+2}$ dimer can be explained on an electrostatic basis. The negative charge in I_3^- is localized principally on these two atoms.[9a, 14] The slight asymmetry in the I-I distances, 2.908(1) and 2.953(1) Å, presumably also reflects the environment and ready deformability of the I_3^- ion. The I-S contacts are illustrated in Figure 2, and the closest distances are in the range 3.636(2) - 3.989(2) Å. These values are typical of the I-S contacts found in $TTF \cdot I_x$ systems. In the more closely packed $TTF \cdot I_{0.7}$ structure, the I-S contacts are as small as 3.53 Å.[4h] As shown in Figure 2, the closest contact between proximate I_3^- ions is 4.335(1) Å.

Electrical Conductivity. The room temperature dc conductivities of two single crystal samples of $TTF \cdot I_3$ were measured parallel to the hexagonal plane and found to have values of 6×10^{-9} Ω^{-1} cm^{-1} and 9×10^{-10} Ω^{-1} cm^{-1}. The dc conductivity of the latter sample was also measured perpendicular to the hexagonal plane. Here the geometry put the precise value of the conductivity beyond the limitations of the instrumentation, although an upper limit of 9×10^{-9} Ω^{-1} cm^{-1} was determined. Finally, a small polycrystalline sample was examined and found to have $\sigma = 8 \times 10^{-10}$ Ω^{-1} cm^{-1}.

CONCLUSIONS

This work shows the high iodine phase of the TTF·I_x system x = 3, to be an integrated stack material with integral formal oxidation states, i.e. $TTF^+I_3^-$. Not surprisingly, such a structure gives rise to high electrical resistivity. As in the case of the other known integral oxidation state tetrathiafulvalenium salts,[4h, i] the structural motif in TTF·I_3 consists of integrated stacks of alternating $(TTF)_2^{+2}$ dimers and pairs of counter anions. Those factors which govern the stability of various possible crystal structures in TTF salts have been discussed at length.[4h, i, 19, 20] It appears that the present structural result can be best rationalized in terms of the electrostatic destabilization with respect to the partially oxidized situation of an integral oxidation state (+1) segregated stack structure.[4h, i, 19] In addition, the close interplanar separation in the $(TTF)_2^{+2}$ suggests enhanced covalent bonding[20, 21] between the cationic moieties in the integral oxidation state case.

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Supplementary Material Available: A listing of structure amplitude tables (21 pages). Ordering information is given on any current masthead page.

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b. Visiting Scientist, Oak Ridge National Laboratory.

c. Present address: Research Laboratories, Eastman Kodak Co., Kodak Park, Rochester, NY 14650.

d. Chemistry Division, Oak Ridge National Laboratory.

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Table 1
Fractional Atomic Coordinates and Anisotropic Thermal Parameters

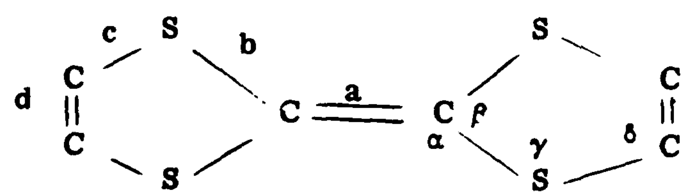
atom	x	y	z	β_{12}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	.34364(5)	-.12731(2)	.62281(6)	.01029(6)	.00230(1)	.01948(10)	.00085(2)	.00253(6)	-.00117(3)
I(2)	.36909(4)	.02401(2)	.70257(5)	.00699(5)	.00205(1)	.01434(8)	.00016(2)	.00241(5)	.00072(2)
I(3)	.37473(5)	.17644(2)	.79679(7)	.01207(2)	.00180(1)	.02430(11)	-.00078(2)	.00441(7)	.00130(3)
S(1)	.2568(2)	.0726(8)	.1492(2)	.0077(2)	.00171(4)	.0188(3)	-.00062(7)	.0035(2)	-.00033(9)
S(2)	.0096(2)	.0611(8)	.3138(2)	.0095(2)	.00188(4)	.0130(3)	.00075(7)	.0036(2)	-.00029(8)
S(3)	-.0098(2)	-.1074(8)	.2256(2)	.0088(2)	.00178(4)	.0148(3)	-.00053(7)	.0032(2)	-.00029(8)
S(4)	.2390(2)	-.0942(8)	.0646(2)	.0082(2)	.00175(4)	.0161(3)	.00062(7)	.0034(2)	.00036(8)
C(1)	.1204(6)	-.0530(3)	.1738(7)	.0060(6)	.00162(14)	.0090(8)	.0005(2)	.0013(6)	-.00070(8)
C(2)	.1306(6)	.0188(3)	.2127(7)	.0056(6)	.00166(14)	.0090(9)	.0001(2)	.0007(6)	.0000(3)
C(3)	2024(8)	.1492(3)	.2370(9)	.0123(10)	.00149(15)	.0199(13)	-.0008(3)	.0010(14)	-.0001(3)
C(4)	.0905(8)	.1434(3)	.3132(9)	.0157(11)	.00157(16)	.0161(12)	.0007(4)	.0024(10)	-.0009(4)
C(5)	0529(8)	-.1848(3)	.1436(9)	.0108(9)	.00154(15)	.0198(14)	-.0005(3)	.0005(10)	.0010(4)
C(6)	.1653(8)	-.1783(3)	.0701(9)	.0123(9)	.00186(17)	.0177(13)	.0007(3)	.0014(10)	-.0001(4)
H(3)	.255(10)	.193(4)	.209(11)						
H(4)	.039(10)	.186(4)	.356(11)						
H(5)	-.006(10)	-.230(4)	.162(11)						
H(6)	.218(10)	-.218(4)	.013(11)						

Table II. Selected Distances and Angles in TTF·I_3

Bond Distances (Å)			
I(1) - I(2)	2.907(1)	S(3) - C(5)	1.743(7)
I(2) - I(3)	2.953(1)	S(4) - C(1)	1.731(6)
S(1) - C(2)	1.715(6)	S(4) - C(6)	1.730(7)
S(1) - C(3)	1.718(7)	C(1) - C(2)	1.382(7)
S(2) - C(2)	1.718(6)	C(3) - C(4)	1.326(11)
S(2) - C(4)	1.724(7)	C(5) - C(6)	1.317(11)
S(3) - C(1)	1.713(6)		
Non-Bonded Contacts (Å)			
I(1) - S(2)′	3.686(2)	I(3) - S(4)	3.870(2)
- S(4)‴	3.832(2)	I(1) - C(1)	3.898(5)
- S(1)″	3.911(2)	I(2) - C(2)	3.955(5)
I(2) - S(3)′	3.881(2)	I(3) - C(4)	3.933(7)
- S(2)′	3.882(2)	I(3) - C(6)	3.902(7)
- S(1)″	3.985(2)	S(1) - S(3)⁗	3.351(2)
- S(4)″	3.946(2)	S(2) - S(4)⁗	3.372(2)
- S(1)‴	3.959(2)	C(1) - C(2)⁗	3.434(7)
- S(4)‴	3.989(2)	C(3) - C(5)⁗	3.424(9)
I(3) - S(3)′	3.637(2)	C(4) - C(6)⁗	3.439(10)
- S(1)″	3.732(2)		
Bond Angles (deg)			
I-I-I	175.39(2)	S(3) - C(1) - S(4)	115.1(2)
S(1) - C(2) - C(1)	122.1(4)	S(1) - C(2) - S(2)	115.7(3)
S(2) - C(2) - C(1)	122.1(4)	C(4) - C(3) - S(1)	116.6(5)
S(3) - C(1) - C(2)	123.3(4)	C(3) - C(4) - S(2)	118.1(5)
S(4) - C(1) - C(2)	121.5(4)	C(6) - C(5) - S(3)	117.0(5)
C(2) - S(1) - C(3)	95.2(3)	C(5) - C(6) - S(4)	117.4(5)
C(2) - S(2) - C(4)	94.2(3)		
C(1) - S(3) - C(5)	95.2(3)		
C(6) - S(4) - C(1)	95.1(3)		

Table III. Dimensions of TTF molecule averaged over assumed mmm molecular symmetry.

	TTF^a 295°K	TTF-TCNQ[b] 298° K	$TTF\cdot I_2$[c] 295° K	$TTF\cdot I_3$[d] 295° K	TTFBr[e]
a	1.349(3)	1.369(4) Å	1.350Å	1.382(7) Å	1.393 Å
b	1.757(2)	1.743(4)	1.732	1.719(8)	1.720
c	1.726(4)	1.736(5)	1.721	1.728(11)	1.724
d	1.314(3)	1.323(4)	1.336	1.322(11)	1.332
α	122.8(2)	122.6(3)	122.9	122.5(8)°	122.3°
β	114.5(2)	114.7(3)	114.3	115.4(4)	115.5
γ	94.4(2)	94.9(3)	95.7	94.9(5)	95.1
δ	118.3(4)	117.6(4)	117.2	117.3(6)	117.2



a Phillips, T. E.; Kistenmacher, T. J.; Ferraris, Cowan, D.O. Chem. Comm. 1973, 14, 471-472.

b Kistenmacher, T. J.; Phillips, T. E.; Cowan, D.O. Acta. Crystallogr, 1974, B30, 763-768.

c Obtained by Fourier refinement and comparable standard errors are unavailable. Ref. 6c.

d This work

e Reference 16.

Table IV. Bond Angles and Distances in Triiodide Ions

$$\mathrm{I} \overset{a}{\text{——}} \mathrm{I} \overset{b}{\text{——}} \mathrm{I}$$
$$\theta$$

	θ(deg)	a(Å)	b(Å)
TTF·I_3 [a]	175.39(2)	2.9533(8)	2.9078(7)
$((C_6H_5)CONH_2)_2H^+I_3^-$ [b]	177.2(5)	2.959(8)	2.900(8)
	176.5(4)	2.943(8)	2.921(8)
$(C_6H_5)_4AsI_3$ [c]	175.61(5)	2.920(2)	2.920(2)
CsI_3 [e]	177.9(1)	3.042(4)	2.840(4)
NH_4I_3 [d]	180.0(1)	3.113(4)	2.791(4)
(thiocarbamato)$_2CuI_3$ [e]	176.5(3)	2.919(7)	2.899(7)
(phenacetin)$_2$·$H^+I_3^-$·I_2 [f]	180	2.907(1)	2.907(1)

[a] This work.

[b] This structure contains parallel chains of triiodide ions, with two types of I_3^- moeties; Reddy, J.M.; Knox, K.; Robin, M.B. J. Chem. Phys., 1964, 40, 1082-1089.

[c] Runsink, J.; Swen-Walstra, S.; Migchelsen, T. Acta. Crystallogr., Sect. B, 1972, 28, 1331-1335.

[d] Cheesman, G.H.; Finney, A.J.T., Acta. Crystallogr., Sect. B, 1970, 26, 904-906.

[e] Wijnhoven, J.G.; Van den Hark, T.E.M.; Beurkeus, P.T. J. Cryst. Mol. Struct., 1972, 2, 189-196.

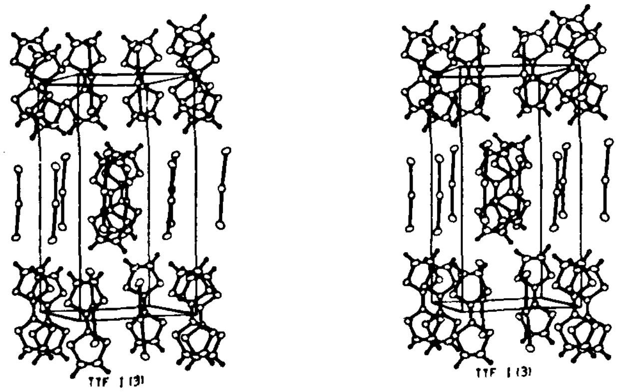
[f] Herbstein, F.H.; Kapon, M. Nature (London), 1972, 239, 153-1954.

FIGURE CAPTIONS

Figure 1. Stereoscopic view of the molecular packing of $TTF \cdot I_3$. The monoclinic b axis is vertical.

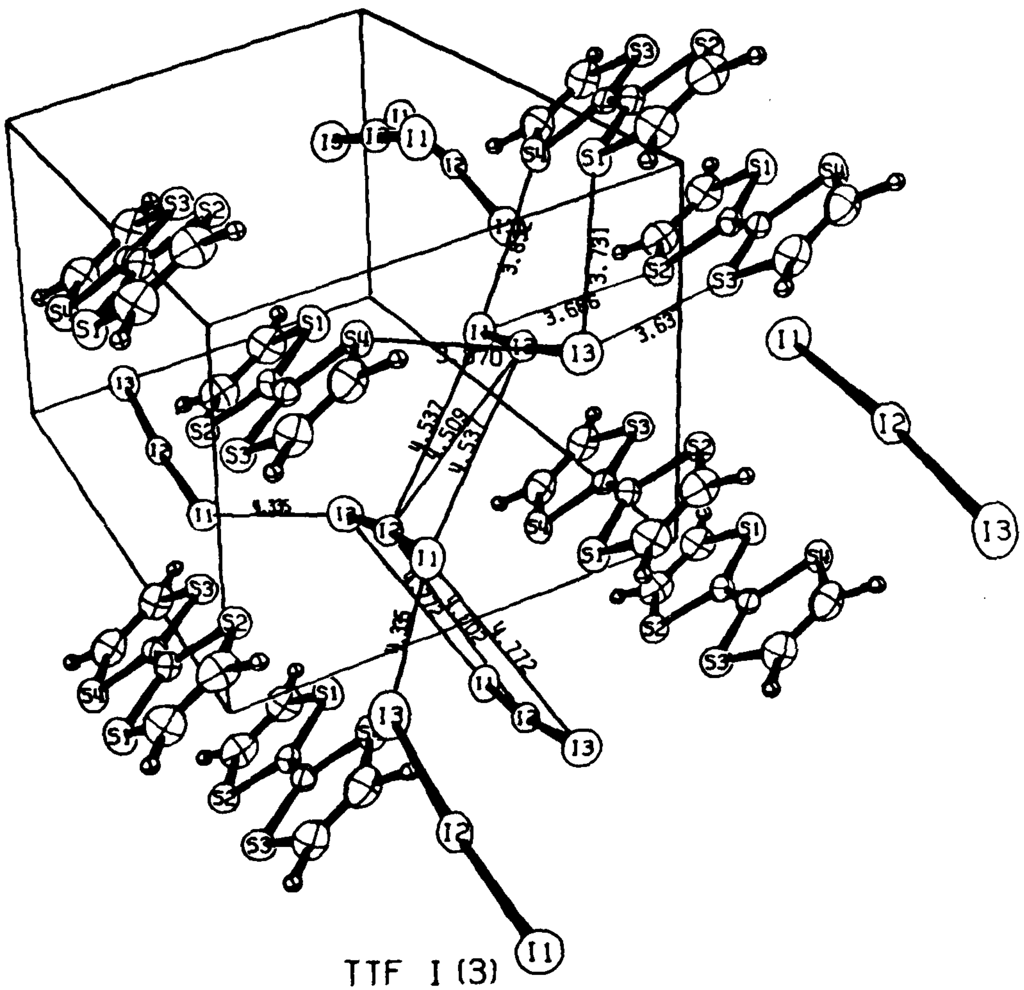
Figure 2. View of stacking within a sheet of $(TTF)_2^{+2}$ dimers and triiodide ions in the ac plane. The zig-zagging triiodide chains along b also are shown.

Figure 3. Bond distances and angles in the TTF^+ ion. Probability ellipsoids (50%) and the numbering scheme are also shown.



TTF I (3)

TTF I (3)



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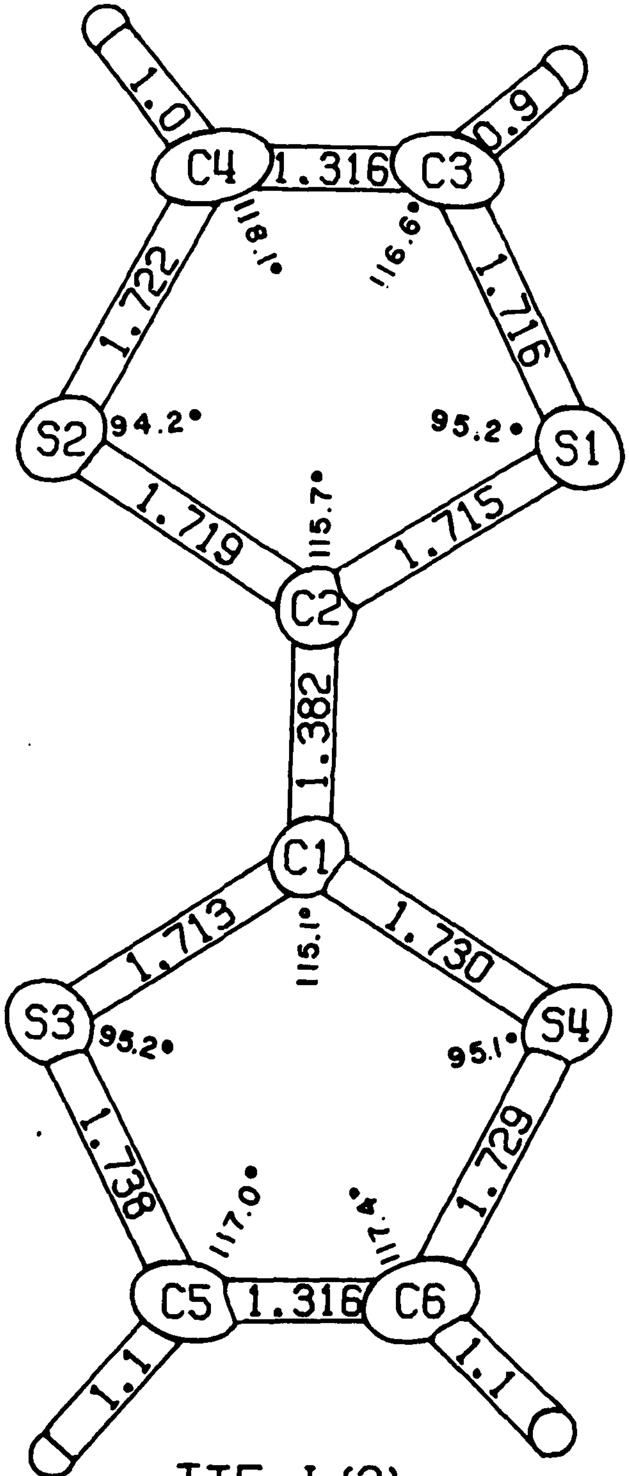

1.0
0.9
C4
1.316
C3
118.1°
116.6°
1.722
1.716
S2
94.2°
95.2°
S1
1.719
115.7°
1.715
C2
1.382
C1
1.713
115.1°
1.730
S3
95.2°
95.1°
S4
1.738
1.729
117.0°
117.4°
C5
1.316
C6
1.1
1.1

TTF I (3)

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